THE MYSTERIOUS CASE OF THE MISSING NH STRETCH TRANSITION

KARL N. BLODGETT, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

The ground and excited state IR vibronic spectra of jet-cooled methyl anthranilate (MA) in the hydride stretch (2400-3800 cm^{-1} and mid-IR (1400-1800 cm^{-1}) regions have been recorded and many of the peaks have been assigned. The key exception, and the subject of this talk, is the H-bonded NH stretch on the S_1 excited surface. In contrast to the S_0 surface, where the NH stretches of -NH_2 can be modeled assuming symmetric and asymmetric stretch vibrations, on the S_1 surface only the free NH stretch is observed. Time-dependent density functional electronic structure calculations combined with both normal mode and VPT2 results predict an extremely bright transition between 2900 cm^{-1} and 3100 cm^{-1} depending on the level of theory for the hydrogen bonded NH stretch. No corresponding transition is observed experimentally. To explain the discrepancy between the experimental and calculated intensities of the dislocated NH stretch transition in the S_1 excited state a model is proposed based on the adiabatic separation of the NH stretch and other internal coordinates. In this model, the excitation of the NH stretch leads to dramatic structural reorganization, this leading to many Franck-Condon factors that, in turn, lead to substantial shared intensity of the initial bright state over hundreds a wavenumbers, thereby diluting the band sufficiently that it is no longer apparent in the spectra.